

THE INFLUENCE OF THE COMBUSTION TEMPERATURE OF THE NON-VOLATILE COMBUSTIBLE WOOD MATTER OF DECIDUOUS TREES UPON ASH PRODUCTION AND ITS PROPERTIES

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ABSTRACT

This paper presents the results of determining the influence of combustion temperature (500–1000 °C) of non-volatile wood matter of deciduous trees Aspen poplar (*Populus tremuloides* Michx.), White birch (*Betula verrucosa* Ehrh.), European beech (*Fagus sylvatica* L.), English oak (*Quercus robur* L.) and Black locust (*Robinia pseudoacacia* L.) upon the production of ash and the content of calcium Ca, magnesium Mg, potassium K and iron Fe.

From the functional dependences between the influence of the combustion temperature of the non-volatile wood matter of the analysed wood species, it follows that the relative decrease in ash content at 1000 °C compared with a burning temperature of 500 °C is less for quaking Aspen poplar at $\Delta A^d = 44.1\%$, for the white birch at $\Delta A^d = 57.8\%$, for European beech at $\Delta A^d = 43.2\%$, for English oak at $\Delta A^d = 43.1\%$ and for Black locust at $\Delta A^d = 34.2\%$.

From determining the concentration of calcium Ca, magnesium Mg, potassium K in ash from the tree species using the ICP AES method, it follows that the highest proportion of ash for combustion temperature $T = 500\text{ °C}$ is in the range of calcium values $X_{Ca} = 221.4\text{--}397.6\text{ g}\cdot\text{kg}^{-1}$, magnesium in ash $X_{Mg} = 25.7\text{--}42.3\text{ g}\cdot\text{kg}^{-1}$, potassium $X_K = 130.5\text{--}199.8\text{ g}\cdot\text{kg}^{-1}$ and iron $X_{Fe} = 1.78\text{--}2.88\text{ g}\cdot\text{kg}^{-1}$. The influence of burning temperature is reflected in the increased concentration of calcium, magnesium and iron in ash and the decreased potassium concentrations in the ash. The decrease potassium in the ash is attributed to evaporation and potassium compounds found in non-volatile combustible of fuel wood.

The decrease in potassium in the combustion process of non-volatile matter of fuel wood also affects the thermal characteristics of the produced ash and according to the criteria for the evaluation of biofuels from in terms of non-sintering ashes from biofuels $(Ca + Mg) / K \geq 1$, contributes towards the stabilisation the creation of ash in crisp form.

Keywords: fuel wood, non-volatile matter, burning temperature, ash, calcium, magnesium, potassium, iron.

INTRODUCTION

Dendromass is formed of natural polymers: cellulose, hemicellulose, and lignin to a lesser extent, of accompanying organic and inorganic (mineral) substances. During their growth, trees obtain mineral substances from the soil via a root system.

The content and concentration of individual elements of mineral substances, as stated by the authors BLAŽEJ *et al.* (1975), SIMANOV (1995), PITMAN (2002), ZULE – DOLENC (2012), DZURENDA *et al.* (2013), HYTÖNEN – NURMI (2015), PÉREZ *et al.* (2015), PŇAKOVIČ – DZURENDA (2015) differ between individual wood species as well as within one wood species, and also markedly depends upon the place of growth and ecological factors. Needles, leaves, bark, wood of branches and roots contain a higher concentration of inorganic substances than the wood of the tree stem. There are also differences related to the age of the tree; young individuals contain a higher concentration of mineral substances than older individuals and, additionally, the wood of deciduous wood species is richer in minerals than the wood of coniferous wood species.

Data on the amount of inorganic substances in dendromass is mainly obtained from indirect determination, i.e. from ash (residue after burning dendromass). In terms of ash production from the combustion process, dendromass ranks amongst fuels with a low ash content with values for dry wood of $A^d = 0.21\text{--}0.67\%$ and bark of $A^d = 1.80\text{--}5.55\%$. According to works by NIKITIN (1956), BUCHANAN (1963), BLAŽEJ *et al.* (1975), MISRA *et al.* (1994), ZEVENHOVEN *et al.* (2010), ash from burning wood is a mixture of oxides: K_2O , Na_2O , CaO , MgO , Fe_2O_3 , Al_2O_3 , SiO_2 , and P_2O_5 . Although the amount and content of ash from dendromass depends upon the wood species and the abovementioned factors, for quantitative representation of individual oxides in ash from wood and bark, BLAŽEJ *et al.* (1975) state the following ranges: $CaO = 40\text{--}70\%$, $K_2O = 10\text{--}30\%$, $MgO = 0.5\text{--}10\%$ and $Fe_2O_3 = 0.5\text{--}2\%$. The inorganic proportion in wood matter determined in ash, according to the works of MISRA *et al.* (1994), MALAŤAK – VACULÍK (2008), ZEVENHOVEN *et al.* (2010), FERNANDES *et al.* (2013), DZURENDA – PŇAKOVIČ (2014) also depends upon the combustion conditions and combustion temperature, biofuel. The proportion of ash decreases with a growth in the combustion temperature of the dendromass. Ash from the combustion process of dendromass below $750\text{ }^\circ\text{C}$ also contains thermally undecomposed carbonates, sulphates and silicates.

The chemical composition of ash has an immediate effect upon the thermal characteristics of ash. According to the works of REZVANI (2003), MALAŤAK and VACULÍK (2008), JANDAČKA *et al.* (2013), DZURENDA – JANDAČKA (2015), the thermal characteristics of ash from biofuel are significantly dependent upon the content of calcium, magnesium and potassium in the ash of biofuel. Whilst the calcium and magnesium compounds increase the melting temperature of ash, potassium compounds with a lower ash softening and melting temperature contribute in decreasing the thermal characteristics of the inorganic residue from burning biofuel.

The aim of the given work is to present the results of the influence of combustion temperature $t = 500\text{--}1000\text{ }^\circ\text{C}$ of the non-volatile combustion matter of aspen poplar, birch, beech, oak and black locust wood upon the production of ash and the quantitative representation of calcium Ca, magnesium Mg, potassium K and iron Fe, i.e. elements with the highest representation in ash and significantly influencing the properties of ash and its form.

EXPERIMENTAL

Samples of fuel wood of wood species: Aspen poplar, White birch, European beech, English oak and Black locust for analysing the influence of the burning temperature of non-volatile combustible matter upon the production and properties of ash were taken from the logs of fuel wood in the dispatch stores of Gabčíkovo and Žarnovica Forest Management.

The density of wood in a dry state was determined in accordance with STN 49 0108:1993 Wood - Determining density. Wood density from the measured weights of samples and their volumes was calculated using the equation:

$$\rho_0 = \frac{m_0}{V_0} \text{ [kg} \cdot \text{m}^{-3}] \quad (1)$$

where: m_0 – weight of the dry sample [kg],
 V_0 – volume of the dry sample [m³].

Determination of the proportion of ash from non-volatile combustible wood matter of the analysed deciduous wood species was carried out by burning samples of dry wood ($W = 0\%$) weighing circa 10 g placed in a ceramic dish in muffle furnace (LAC LMH 04/12). Burning wood in the first phase at temperature $t = 500\text{ }^\circ\text{C}$ was carried out by even heating of the wood sample at a rate of $8\text{ }^\circ\text{C}/\text{min}$ for 60 min. and subsequent maintenance of this temperature in the muffle furnace for a further 450 min. A similar method was used for burning temperatures $t = 600\text{ }^\circ\text{C}$ to $1000\text{ }^\circ\text{C}$. In the first phase of burning, the wood sample was heated to $500\text{ }^\circ\text{C}$ at a rate of $8\text{ }^\circ\text{C}/\text{min}$ and was maintained at this temperature for a further 30 min. In the second phase, we proceeded in heating the non-volatile combustible matter of the sample for 60 min. to the required temperature and this temperature was maintained in the muffle furnace for 360 min. (fig. 1). The content of ash A^d was calculated using the equation:

$$A^d = \frac{(m_3 - m_1)}{m_2 - m_1} \cdot 100 \text{ [%]} \quad (2)$$

where: A^d - ash content in the fuel [%],
 m_1 - weight of the empty dish [g],
 m_2 - weight of the dish with the fuel sample [g],
 m_3 - weight of the dish with the ash [g].

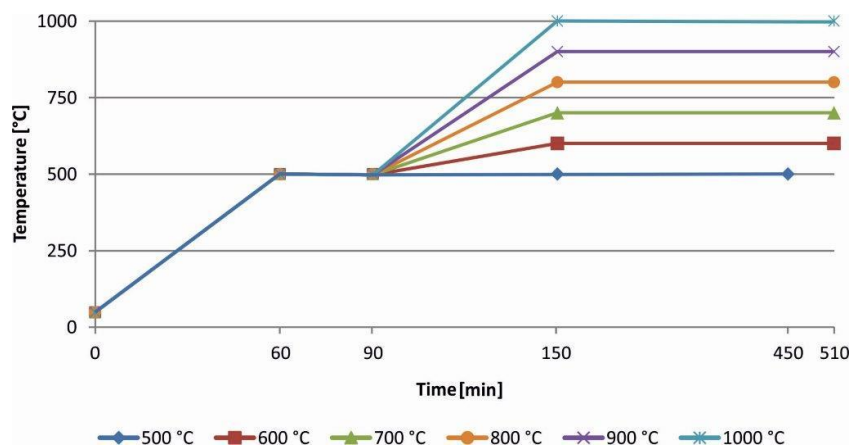


Fig. 1 The development of the heating temperature and burning of a sample of biofuel in a muffle furnace.

The concentration of calcium Ca, magnesium Mg, potassium K and iron Fe in ash was determined from samples of ash from the process of burning aspen poplar, beech and black locust wood at temperatures from $500\text{ }^\circ\text{C}$ to $1000\text{ }^\circ\text{C}$ in a muffle furnace using the AES ICP method. The principle of the AES ICP method is based on measuring the atomic emissions of individual elements using optical spectroscopy using an ES 725 VARIAN atom emission spectrometer with inductively coupled plasma.

The content of calcium Ca, magnesium Mg, potassium K and iron Fe in ash from the given wood species is stated using equation (3), i.e. calculating the given element in ashes for the production of ash from 1 kg of dry wood.

$$X_i = \frac{A_{ti} \cdot X_{A_{ti}}}{100} \text{ [g} \cdot \text{kg}^{-1}] \quad (3)$$

where: A_{ti} – proportion of ash from the sample of wood from the given wood species [%],
 $X_{A_{ti}}$ – concentration $X_{A_{ti}}$ of the element in ash from the sample of wood from the given wood species [$\text{g} \cdot \text{kg}^{-1}$].

RESULTS AND DISCUSSION

Density of wood of wood species: Aspen poplar, White birch, European beech and the core wood of English oak and Black locust in a dry state is shown in Table 1.

Tab. 1. Densities of dry wood of the analysed wood species.

Fuel wood of wood species	The basic statistical characteristics of the density of wood in a dry state			
	ρ_0 [$\text{kg} \cdot \text{m}^{-3}$]	s [$\text{kg} \cdot \text{m}^{-3}$]	v_x [%]	n [-]
Aspen poplar	398.2	17.8	4.5	17
White birch	608.3	32.2	5.3	16
European beech	678.8	26.1	3.9	15
English oak	718.8	34.5	4.8	17
Black locust	721.8	23.4	3.2	16

The densities of dry wood of the analysed wood species can be said to be the average values of densities of wood of the given wood species growing in Slovak territory, which is also proven by the works of REGINÁČ *et al.* (1990), POŽGAJ *et al.* (1997), BANSKI – DZURENDA (2014). The given statement also indirectly declares the fact that fuel wood, used for the preparation of samples for analysing the influence of combustion temperature upon the production of ash, is wood undamaged by mould or contaminated with foreign substances.

The results of laboratory works determining the proportion of ash from burning wood of the analysed wood species at temperatures $t = 500$ °C to 1000 °C are shown on Fig. 2.

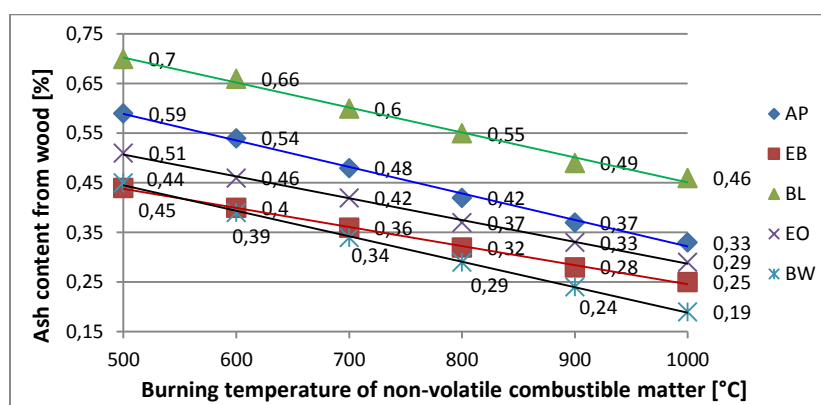


Fig. 2 Ash depending upon the wood species: Aspen poplar (AP), White birch (BW), European beech (EB), English oak (EO), Black locust (BL).

Functional dependences of ash content from burning aspen poplar, birch, beech, oak and black locust wood in a muffle furnace with a combustion temperature from $t = 500$ – 1000 °C are shown in Table 2.

Tab. 2 Functional dependencies of burning temperature upon the production of ash.

Wood species	Functional dependence	Determination coefficient
<i>Aspen poplar</i>	$A^d = -0.0005 \cdot t + 0.8557$	$R^2 = 0.9961$
<i>White birch</i>	$A^d = -0.0005 \cdot t + 0.7024$	$R^2 = 0.9990$
<i>European beech</i>	$A^d = -0.0004 \cdot t + 0.6310$	$R^2 = 0.9982$
<i>English oak</i>	$A^d = -0.0004 \cdot t + 0.7267$	$R^2 = 0.9984$
<i>Black locust</i>	$A^d = -0.0005 \cdot t + 0.9538$	$R^2 = 0.9937$

The results of analyses stating the proportion of ash from burning the non-volatile combustible matter of the analysed deciduous wood species have been confirmed by current knowledge of the low proportion of ash from wood presented in the works of SIMANOV (1995), GEFFERTOVÁ – GEFERT (2003), VESTERINEN (2003), JANDAČKA *et al.* (2007), MALATAK – VACULIK (2008), Dzurenda *et al.* (2013) and at the same time, they show a certain dispersity of values of inorganic residue within a wood species, induced by its thermal decomposition. The inorganic proportion of wood is highly heterogenic and mainly formed of carbonates and sulphates, CaCO_3 , MgCO_3 , FeCO_3 , CaSO_4 , MgSO_4 , which, at individual temperatures, decompose with varying intensity into carbon dioxide CO_2 and the appropriate metal oxides. This is also confirmed by our analysis of the proportion of calcium carbonate CaCO_3 in ash from black locust wood, according to which, at burning temperature of $t = 500$ °C, the ash contained 78 % calcium carbonate CaCO_3 , at burning temperature $t = 700$ °C the value of calcium carbonate decreased to 66 % and at burning temperature $t = 800$ °C the proportion of calcium carbonate CaCO_3 in the ash decreased to 13 %. Another thermal process contributing to a decrease in the proportion of ash, according to the works of SIPPULA *et al.* (2007), TISSARI (2008), is the evaporation of potassium compounds K_2CO_3 , KCl and K_2SO_4 .

Determining the functional dependences between a decrease in the content of ash and the combustion temperature of the non-volatile combustible matter of aspen poplar, birch, beech, oak and black locust wood can be considered as a contribution towards widening current knowledge since it can be used for energy, environmental and ecological analysis of biofuel dependent upon the proportion of ash created in the combustion process. Non-consideration of the stated fact when calculating the production of ash from energy equipment burning, for example, black locust fuel wood is expressed by an relative error ($\Delta A^d = \frac{A_{t=550}^d - A_{t=815}^d}{A_{t=550}^d} * 100$) in the amount of 19.6 % if the inorganic proportion is determined in compliance with *EN 14775:(2010)* at a temperature of $t = 550$ °C, or *ISO 1171:(2003)* at a temperature of $t = 815$ °C.

The concentration of calcium Ca, magnesium Mg, potassium K and iron Fe, determined using the AES ICP method, in ash from burning aspen poplar, beech and black locust wood at temperatures from 500 °C to 1000 °C in a muffle furnace is shown on Fig. 3–6.

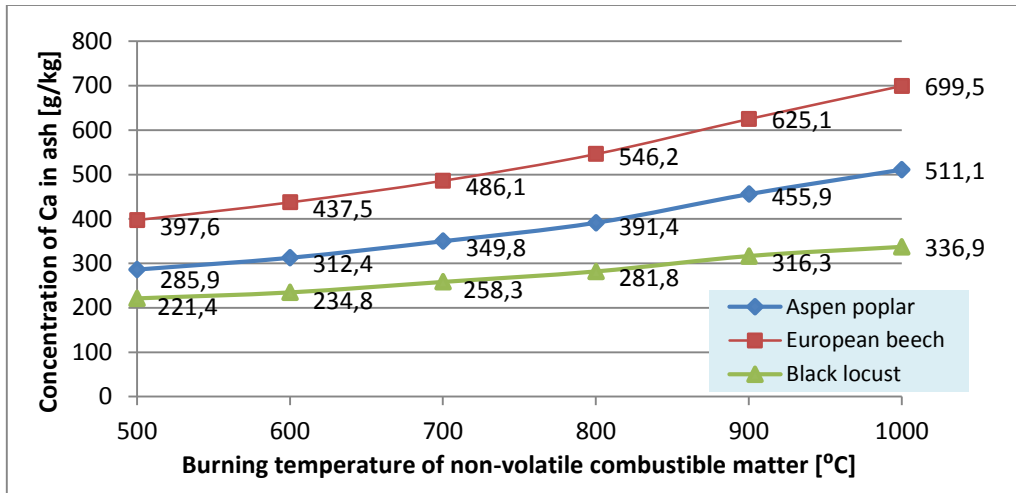


Fig. 3 The concentration of calcium in ash from the analysed wood species from wood.

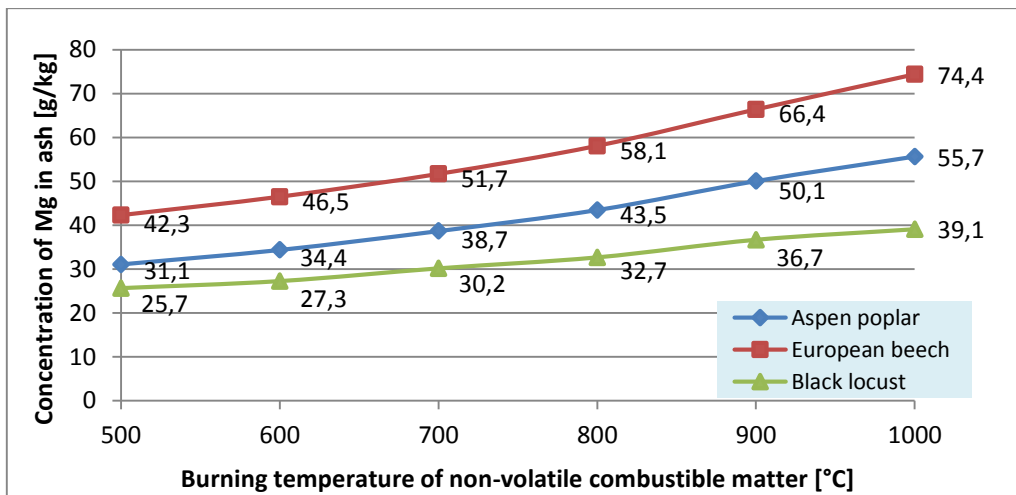


Fig. 4 The concentration of magnesium in ash from the analysed wood species from wood.

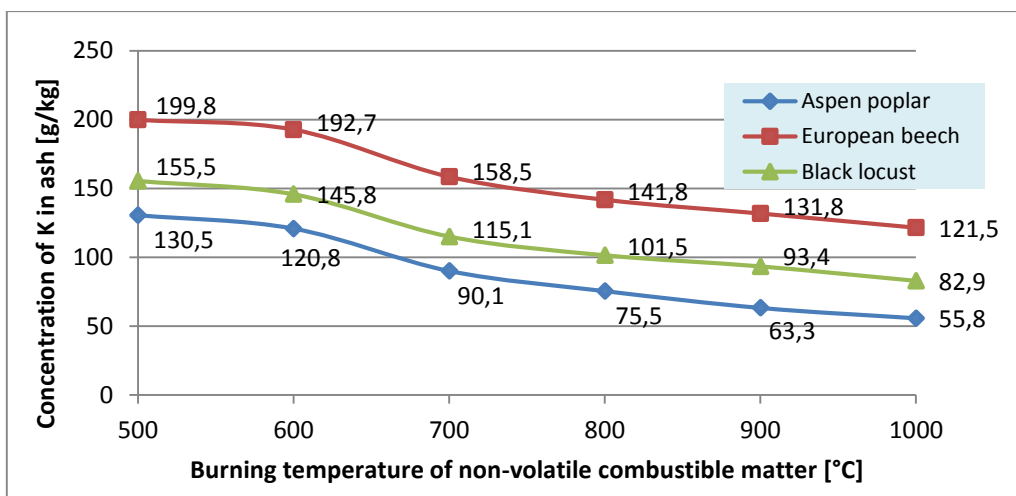


Fig. 5 The concentration of potassium in ash from the analysed wood species from wood.

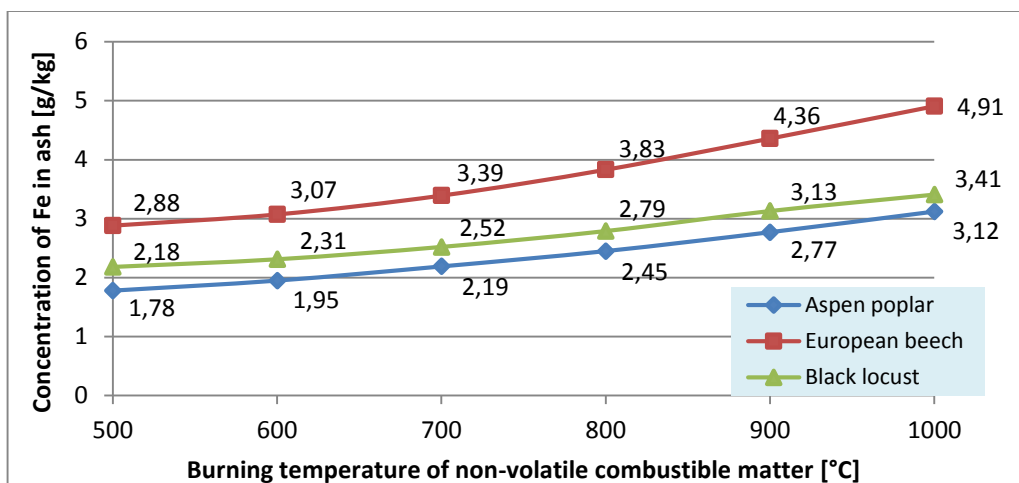


Fig. 6 The concentration of iron in ash from the analysed wood species from wood.

The content of calcium Ca, magnesium Mg, potassium K and iron Fe in ash from the process of burning 1 kg of dry wood of the given wood species, calculated using equation (3), at temperatures of 500–1000 °C is shown in Tab. 3. and Fig. 7.

Tab. 3 The content of calcium, magnesium, potassium and iron in ash [g·kg⁻¹].

Burning temperature [°C]	The content of inorganic elements in ash from the process of burning 1kg of fuel wood at temperatures of 500 – 1000 °C [g.kg ⁻¹]											
	Poplar wood				Beech wood				Black locust wood			
	Ca	Mg	K	Fe	Ca	Mg	K	Fe	Ca	Mg	K	Fe
500	1.686	0.184	0.769	0.011	1.749	0.186	0.880	0.013	1.550	0.179	1.088	0.015
600	1.687	0.185	0.652	0.011	1.750	0.186	0.719	0.012	1.549	0.180	0.962	0.015
700	1.679	0.186	0.432	0.011	1.749	0.186	0.571	0.012	1.549	0.181	0.691	0.015
800	1.683	0.187	0.325	0.011	1.747	0.185	0.454	0.013	1.550	0.179	0.558	0.015
900	1.687	0.185	0.234	0.010	1.750	0.185	0.369	0.012	1.549	0.179	0.457	0.015
1000	1.686	0.184	0.184	0.010	1.748	0.186	0.304	0.012	1.549	0.179	0.381	0.016
Average value	1.686	0.185	---	0.011	1.749	0.186	---	0.012	1.549	0.179	---	0.015
Standard deviation	0.003	0.001	---	0.001	0.001	0.001	---	0.001	0.001	0.001	---	0.001

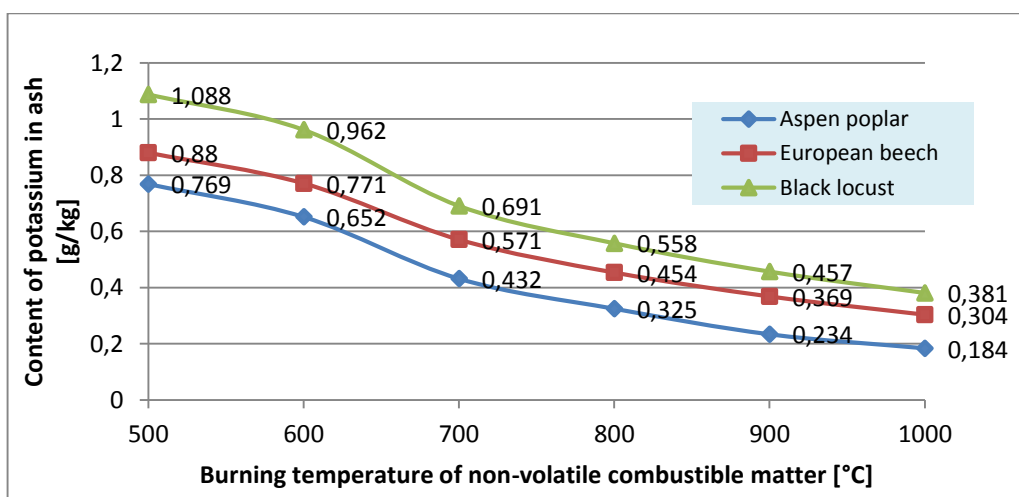


Fig. 7 The content of potassium in ash from 1 kg of dry wood of the analysed wood species.

From analysis of the concentration of calcium Ca, magnesium Mg, potassium K and iron Fe in ash from the non-volatile combustible wood matter of wood species: Aspen poplar, European beech and Black locust burned in a muffle furnace at $t = 500\text{ }^{\circ}\text{C}$, it is clear that calcium has the highest content in ash at $X_{\text{Ca}} = 221.4\text{--}397.6\text{ g}\cdot\text{kg}^{-1}$. Compared to calcium, the concentrations of magnesium, potassium and iron are significantly lower: $X_{\text{Mg}} = 25.7\text{--}42.3\text{ g}\cdot\text{kg}^{-1}$, $X_{\text{K}} = 130.5\text{--}199.8\text{ g}\cdot\text{kg}^{-1}$ and $X_{\text{Fe}} = 1.78\text{--}2.88\text{ g}\cdot\text{kg}^{-1}$. The ratio of the average content of calcium Ca, magnesium Mg, potassium K and iron Fe in ash from wood of the analysed wood species is $\text{Ca} : \text{Mg} : \text{K} : \text{Fe} = 1 : 0.11 : 0.54 : 0.01$ i.e. compared to calcium, there is 9.1 times less magnesium, 1.86 time less potassium and 100 times less iron. The ratio of the content of calcium Ca, magnesium Mg, potassium K and iron Fe in ash from the wood of wood species: Aspen poplar, European beech and Black locust is similar to the ratio of these elements in ash matter (inorganic proportion of wood) of deciduous wood species stated in EN 14961-1 Solid biofuel.

The influence of an increased burning temperature of the non-volatile combustible wood matter is expressed in the increased concentrations of calcium, magnesium and iron and the decrease in the concentration of potassium in the ash. An increase in the concentration of calcium Ca, magnesium Mg and iron Fe in ash closely corresponds to the decrease in the production of ash at individual burning temperatures of non-volatile combustible matter. This is confirmed by the content of these elements in ash stated in Tab. 3, which closely correlates with the average value of the given element in the ash. The given statement is unrelated to the presence of potassium in the ash from the combustion process of non-volatile combustible matter in aspen poplar, beech and black locust wood. Concentrations of potassium as well as the content of potassium in ash from the wood of the analysed wood species decreases with an increase in the burning temperature of non-volatile combustible wood matter. The stated fact attributed to the evaporation of potassium compounds K_2CO_3 , KCl , K_2SO_4 and the creation of PM emissions in the form of fine ash extracted with combustion gases SIPPULA *et al.* (2007), TISSARI (2008).

A decreased concentration of potassium in ash has a positive impact upon the stability of the creation of ash in the form of loose matter without slag. In terms of slagging ash from biofuel $(\text{Ca} + \text{Mg}) / \text{K} \geq 1$, DZURENDA – JANDAČKA (2015), ash from burning biofuel with a ratio of total of calcium Ca and magnesium Mg to potassium K greater than 1 does not sinter and is in the form of loose matter on the boiler's grid under an oxidation temperature of $t \leq 1100\text{ }^{\circ}\text{C}$. The value of the stated criterion for ash from aspen poplar, beech and black locust wood at burning temperature $t = 500\text{ }^{\circ}\text{C}$ is $(\text{Ca} + \text{Mg}) / \text{K} = 1.90\text{--}2.43$ and at burning temperature $t = 1000\text{ }^{\circ}\text{C}$, the given ratio increases to $(\text{Ca} + \text{Mg}) / \text{K} = 6.36\text{--}12.96$. Non-slagging of ash from the wood of the analysed wood species was also confirmed by experiments on burning non-volatile combustible matter from which the ash was always in loose form.

CONCLUSION

The results of experiments determining the influence of burning temperature of the non-volatile combustible matter of the wood of deciduous wood species in a muffle furnace upon the production of ash confirm current knowledge about the low production of ash by the wood, and specify the functional dependences between the influence of temperature at intervals of $t = 500\text{--}1000\text{ }^{\circ}\text{C}$ upon the production of ash from the wood of wood species: Aspen poplar, White birch, European beech, English oak and Black locust.

Non-consideration of the stated facts when calculating the production of ash from energy equipment burning fuel wood is loaded with a not-insignificant error. For example, if the inorganic proportion from black locust wood is determined in compliance with EN 14775:(2010) at burning temperature $t = 550\text{ }^{\circ}\text{C}$, or ISO 1171:(2003) at burning temperature $t = 815\text{ }^{\circ}\text{C}$, an error is created at a level of 19.6 %.

Qualitative and quantitative analyses of ash show that an increase in the burning temperature of the non-volatile combustible matter of fuel wood of deciduous wood species: Aspen poplar, European beech and Black locust causes an increase in the concentration of calcium Ca, magnesium Mg and iron Fe proportionate to the decrease in the production of ash and the concentration of potassium K in the ash decreases. A decrease in the concentration of potassium in the process of burning the non-volatile combustible matter of fuel wood positively influences the thermal characteristics of the created ash and contributes towards stabilising the creation of ash in the form of loose matter.

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